Claims

1. A method for the heat treatment of shaped bodies made of a superconducting material based on (Y/Rare Earth)BaCuO, characterised in that a coating consisting of a coating material is applied to at least one part of at least one surface of the shaped body, whereby the coating material melts at least partially at a lower temperature than the material of the shaped body or/and is flowable at a lower temperature than that material, whereby the shaped body together with the applied coating material is heated to a temperature at which the material of the shaped body does not yet melt or/and is not yet flowable but at which the coating material is at least partially softened by the heat or/and is in a flowable state, and whereby at least one part of a region of the shaped body located near the surface is modified at this temperature or/and during a succeeding cooling process, and wherein the shaped body treated in such a manner is enriched with oxygen during the cooling process or/and during a succeeding heat treatment whereby the modification contributes to the increase in remanent induction or/and to the increase in the critical current density of the shaped body enriched with oxygen.

2. A method in accordance with Claim 1, characterised in that the superconducting material contains at least one Rare Earth element including lanthanum and yttrium and also at least barium, copper and oxygen and possibly elements selected from the group consisting of Be, Mg, Ca, Sr, Zn, Cd, Sc, Zr, Hf, Pt, Pd, Os, Ir, Ru, Cu, Ag, Au, Hg, Tl, Pb, Bi and S.

3. A method in accordance with at least one of the preceding Claims, characterised in that the shaped body of the superconducting material was produced by a melt-texturising process, by a zone-melting process, by a single crystal growth process or by producing a texturised polycrystalline superconducting material.

4. A method in accordance with at least one of the preceding Claims, characterised in that, prior to or/and after the

modification thereof, the shaped body of the superconducting material comprises one to one hundred grains or/and one to one hundred domains, preferably just one grain and up to four domains.

5. A method in accordance with at least one of the preceding Claims, characterised in that the untreated or/and the treated shaped body of the superconducting material, the coating material or/and the layer of material includes phases which are selected from the group of phases corresponding to an approximate composition of $Y_1Ba_2Cu_3O_v$, $Y_2Ba_1Cu_1O_w$, $Yb_1Ba_2Cu_3O_{v'}$, $Yb_2Ba_1Cu_1O_{w'}$, $Er_1Ba_2Cu_3O_{v'}$, $Er_2Ba_1Cu_1O_{w'}$, $Sm_1Ba_2Cu_3O_{v''}$, $Sm_2Ba_1Cu_1O_{w''}$, $Nd_1Ba_2Cu_3O_{v'''}$, $Nd_4Ba_2Cu_2O_{w'''}$, Y_2O_3, CeO_2, Pt, PtO_2, Ag and AgO_2, where Y, Yb, Sm or/and Nd may also be partially substituted by other lanthanides or Y, and wherein other related chemical elements may occur in Ag or/and AgO_2.

6. A method in accordance with at least one of the preceding Claims, characterised in that the untreated or/and the treated shaped body of the superconducting material, the coating material or/and the layer of material comprise calcium or/and other cations which alter the band structure of the electrons and contribute to the higher critical transport current densities.

7. A method in accordance with at least one of the preceding Claims, characterised in that the shaped body of the superconducting material or/and the coating material comprise at least one gradient in regard to the chemical composition, the grain structure or/and the peritectic flow or melting temperatures.

8. A method in accordance with at least one of the preceding Claims, characterised in that the coating material is applied such as to have a layer thickness in the range from 1 µm to 5 mm, preferably 10 µm to 3 mm, and especially preferred from 50 µm to 2 mm.

9. A method in accordance with at least one of the preceding Claims, characterised in that the coating material is applied in the form of a powder, a shaped body or/and a coating - the powder preferably being a powder mixture or in granular form, the shaped body is preferably a compressed, a calcinated, a sintered or a molten shaped body, and the coating is preferably in the form of a physically or/and a chemically deposited coating that is basically produced by precipitation, sputtering or spray-pyrolysis.

10. A method in accordance with at least one of the preceding Claims, characterised in that a powder-like coating material is applied, that a shaped body of the coating material is placed on the corresponding surface of the shaped body of the superconducting material, or/and that the coating process is effected from the gas phase, from a solution or suspension or by using an aerosol.

11. A method in accordance with at least one of the preceding Claims, characterised in that the coated shaped body of the superconducting material is maintained at a temperature corresponding to Claim 1 until such time as a part of the coating material penetrates or diffuses into the superconducting material.

12. A method in accordance with at least one of the preceding Claims, characterised in that, during the modification of the superconducting material, a gradient is produced in the shaped body of the superconducting material or/and in the layer of material produced from the coating material.

13. A method in accordance with at least one of the preceding Claims, characterised in that the residual crystal nuclei, the layer of material or/and the uneven surface of the shaped body is mechanically removed after the modification of the superconducting material, and in that the shaped body is subjected thereafter to a heat treatment if necessary.

14. A method in accordance with at least one of the preceding Claims, characterised in that a shaped body of the superconducting material is produced substantially in the form of plates, solid cylinders, hollow cylinders, rings, discs, bars, tubes, wires, tapes or coils.

15. A method in accordance with at least one of the preceding Claims, characterised in that the shaped body of the superconducting material is in direct contact only with a superconducting material based on (Y/Rare Earth)BaCuO and, possibly, with a coating material during the firing and heat treatments.

16. A method in accordance with at least one of the preceding Claims, characterised in that a large-sized shaped body of the superconducting material comprises a plurality of mutually spaced crystal nuclei whose c-axes are oriented along one of the main axes or main directions of the geometry of the shaped body or are at right angles thereto.

17. A method in accordance with at least one of the preceding Claims, characterised in that a large-sized shaped body of the superconducting material is produced in a plurality of segments, which are jointed together if necessary, especially by heat treatment at a temperature corresponding to Claim 1, possibly by the application of pressure and possibly by the addition of a coating material to the boundary surfaces that are to be jointed together.

18. A shaped body of a superconducting material based on (Y/Rare Earth)BaCuO which is obtainable by a method in accordance with at least one of the Claims 1 to 17, characterised in that it contains at least one Rare Earth element selected from the group consisting of Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and in that it has a maximum value of remanent induction at 77 K and 0 T of at least 1100 mT, preferably of at least 1200 mT, and even more particularly preferred of at least 1300 mT, and above all of more than 1400 mT.

19. A shaped body in accordance with Claim 18, characterised in that the alignment of the c-axes of the grains or of the one grain of a cylinder, a ring, a tube or a disc consisting substantially of one or more segments is substantially in line with the axis of the cylinder / the axis of the plate, or another main direction of the shaped body, or, it is at right angles thereto.

20. A shaped body in accordance with Claim 18 or 19, characterised in that it substantially comprises a composition of $(Y/Rare\ Earth)_1Ba_2Cu_3O_x$ where x lies in the range from 6.5 to 7 and wherein Y or/and Rare Earth may be in excess.

21. A shaped body in accordance with at least one of the Claims 18 to 20, characterised in that it consists to more than 60 Vol.-% and preferably to more than 80 Vol.-% of one phase of the composition $(Y/Rare\ Earth)_1Ba_2Cu_3O_x$ where x lies in the range from 6.5 to 7, preferably to more than 90 %, and particularly preferred to more than 95 %.

22. A shaped body in accordance with at least one of the Claims 18 to 21, characterised in that it has a critical transport current density of at least 4 10^4 A/cm^2 in the external field of 1 T at 77 K, preferably of at least 6 10^4 A/cm^2, and particularly preferred of at least 8 10^4 A/cm^2.

23. A shaped body in accordance with at least one of the Claims 18 to 22, characterised in that it has a fracture toughness as determined by the fracture system about the hardness impressions of at least 1 Mpa $\sqrt{m}$, preferably of at least 1.5 Mpa $\sqrt{m}$.

24. The use of a shaped body consisting of a superconducting material produced in accordance with any of the Claims 1 to 17 on the basis of (Y/Rare Earth)BaCuO, for transformers, current breakers, power leads, magnetic screenings, magnetic bearings or/and as magnets, especially as cryogenic bearings, in flywheel storage devices, in particle accelerators, in the rotors of electrical machines.

25. The use of a shaped body consisting of a superconducting material in accordance with any of the Claims 18 to 23 for transformers, current breakers, power leads, magnetic screenings, magnetic bearings or/and as magnets, especially as cryogenic bearings, in flywheel storage devices, in particle accelerators, in the rotors of electrical machines.

Drawings

Sheet 1/3

Prior to infiltration

Following infiltration

Sheet 2/3

Increase of remanent induction by Yb- infiltration

Prior to infiltration

Following infiltration

Sheet 3/3

Shaped body texturised by the modified TSMG process but not subjected to an infiltration post-treatment

Amended pages

Claims

1. A method for the heat treatment of shaped bodies made of a superconducting material based on (Y/Rare Earth)BaCuO, characterised in that a coating consisting of a coating material is applied to at least one part of at least one surface of the shaped body, whereby the coating material melts at least partially at a lower temperature than the material of the shaped body or/and is flowable at a lower temperature than that material, whereby the shaped body together with the applied coating material is heated to a temperature at which the material of the shaped body is at least partially softened by heat or/and is in a flowable state, and whereby at least one part of a region of the shaped body located near the surface is modified at this temperature or/and during a succeeding cooling process, in that the coating material completely or at least partially infiltrates the region of the shaped body located near the surface, and wherein the shaped body treated in such a manner is enriched with oxygen during the cooling process or/and during a succeeding heat treatment whereby the modification contributes to the increase in remanent induction or/and to the increase in the critical current density of the shaped body enriched with oxygen.

22. A shaped body in accordance with at least one of the Claims 18 to 21, characterised in that it has a critical transport current density of at least 4×10^4 A/cm^2 in the external field of 1 T at 77 K, preferably of at least 6×10^4 A/cm^2, and particularly preferred of at least 8×10^4 A/cm^2.

Translator's note: Hereinafter, the curly brackets { } denote associated text which is not on these amended pages but is required to locate/clarify the beginning and/or ending of the pages in the context of the full translation.

Page 4
{An enlargement of the magnetic domains without increasing the size of the shaped body can also be achieved in the case of shaped bodies incorporating cracks or/and other point defects by healing such point defects using the method described in the German patent application 198 41 925.2. } By virtue of the reference thereto, {this} patent application is considered to be included in full in the present application.

Furthermore, shaped bodies based upon SmBaCuO are known from Ikuta et al., Supercond. Sci. Techn. 11, 1998, 1345 - 1347, these bodies containing a high proportion of Ag_2O and having a remanent induction of up to 1700 mT. However, such an Sm-rich superconducting material can only be produced with great difficulty and in the absence of air since the superconducting phase Sm-123 is not stable under such conditions. The production of the shaped body must therefore be undertaken in a protective gas atmosphere having a very low partial pressure of oxygen. Furthermore, a comparison with YBaCuO type shaped bodies was drawn in Figure 2 of this publication, the remanent induction thereof being not even half as large as that of shaped bodies based upon SmBaCuO.

Consequently, the object of the invention is to propose a method by means of which such superconducting materials having a high remanent induction, a high levitation force or/and a high critical transport current density can be produced. Furthermore, it is advantageous if these shaped bodies can be produced in as simple and reliable a manner as possible.

This object is achieved by a method for the heat treatment of shaped bodies made of a superconducting material based on (Y/Rare Earth)BaCuO, which is characterised in that a coating consisting of a coating material is applied to at least one part

of the surface of the shaped body, whereby the coating material melts at least partially at a lower temperature than the material of the shaped body or/and is flowable at a lower temperature than that material and, possibly hereby, flows out over the surface of the shaped body, whereby the shaped body together with the applied coating material is heated to a temperature at which the material of the shaped body does not yet melt or/and is not yet flowable but at which the coating material is at least partially softened by the heat or/and is in a flowable state, and whereby at least one part of a region of the shaped body located near the surface is modified at this temperature or/and during a succeeding cooling process in that the coating material infiltrates partially or at least partially into the region of the shaped body located near the surface, and wherein the shaped body treated in such a manner {is enriched with oxygen during the cooling process or/and during a succeeding heat treatment whereby the modification contributes to the increase in remanent induction or/and to the increase in critical current density of the shaped body enriched with oxygen.}

Page 19

{Preferably, the shaped body is a cylinder, a ring, a tube or a disc consisting substantially of one or more segments wherein the} alignment of the c-axes of the grains or of the one grain is substantially in line with the axis of the cylinder / the axis of the plate, or with another main direction of the shaped body, or, it is at right angles thereto.

The shaped body may be characterised in that it substantially comprises a composition of (Y/Rare Earth)$_1Ba_2Cu_3O_x$ where x lies in the range from 6.5 to 7 and wherein Y or/and Rare Earth may be in excess. It advantageously consists to more than 60 Vol.-%, and particularly preferred, to more than 70 or to more than 80 Vol.-% of one phase of the composition (Y/Rare Earth)$_1Ba_2Cu_3O_x$ where x lies in the range from 6.5 to 7. If the component of the 211-phase is too small however, then the superconducting properties may become worse.

The shaped body may have a critical transport current density of at least 4 x 10^4 A/cm^2 in the external field of 1 T at 77 K, preferably of at least 6 x 10^4 A/cm^2, and particularly preferred of at least 8 x 10^4 A/cm^2, but more especially, of at least 9.7 10^4 A/cm^2. It may also have a fracture toughness as determined by the fracture system about the hardness impressions of at least 1 Mpa $\sqrt{m}$, preferably of at least 1.5 Mpa $\sqrt{m}$. Furthermore, it may have a bending strength of at least 300 Mpa and preferably of at least 400 Mpa.

By virtue of the method in accordance with the invention, it was possible, without problems, to modify (= to heat treat) single domain shaped bodies having a diameter of e.g. 45 mm and a height of 12 mm as well as those in the form of e.g. 40 x 40 x 12 mm square plates.

The shaped bodies produced in accordance with the invention may be made use of, for example, in transformers, current breakers, power leads, magnetic screenings, magnetic bearings or/and as magnets utilisable for different purposes.

Page 20

Drawings:

The Figures depict the distribution of the magnetic remanent induction in respect of Example 1. Figures 1 and 3 indicate the test results for the preliminary material and Figures 2 and 4 the test results for the superconducting material that has been heat treated in accordance with the invention.

Examples:

The test methods will be explained hereinafter and the invention will be presented in exemplary manner on the basis of selected embodiments:

Test methods:

Measuring the distribution of the remanent magnetic field:

The superconducting shaped body that is to be magnetised was firstly raised to temperatures above its transition temperature in the field of a conventional electromagnet. Hereby, the magnetic field penetrated completely into the shaped body which is not superconducting in this state. The superconducting shaped body was then cooled to below its transition temperature T_c, in general at approximately 77 K, and thereafter, the field of the electromagnet was completely run down. A portion of the magnetic flux, the remanent induction, thereby remained frozen in the superconductor. The measurement of the distribution of this remanent induction was effected by scanning the surface of the shaped body by means of a micro-Hall-probe type HHP-VA from the company Arepoc. The active surface of the probe was usable down to a temperature of 4.2 K. The measurements were usually only carried out at 77 K. In order to prevent the probe from coming into contact with the surface of the shaped body during the measurement, it was kept recessed into a PTFE mounting. The minimum spacing between the probe and the surface of the shaped body during the measurement thereby amounted to 0.3 mm. The

maximum value of the remanent induction was detected at this spacing. The scanning of the surface of the shaped body for determining the distribution of the remanent induction was carried out at a spacing of 0.5 mm.

Page 23

3. a dwell period of 25 h at 960 °C
4. cooling over 70 h to 890 °C at a cooling rate of 1 K/h
5. cooling over 25 h to 20 °C.

The measured distribution of the remanent induction hereby produced after the infiltration process (= heat treatment) resulted in a maximum value of $B_{z,max}$ of 1026 mT (Figure 2).

Example 2:

As in Example 1, a texturised shaped body having dimensions of 38 x 38 x 12 mm^3 was produced. However, diverging from Example 1, Er-123 was used as the coating material. The distribution of the remanent induction following the texturising process resulted in a maximum value $B_{z,max}$ of the remanent induction of 902 mT (Figure 3).

The shaped body together with the coating material was then subjected to the following temperature treatment:

1. heating over 12 h to 900 °C
2. heating over 3 h to 980 °C
3. a dwell period of 3 h at 980 °C
4. cooling over 2 h to 970 °C
5. a dwell period of 10 h at 970 °C
6. cooling over 60 h to 900 °C
7. cooling over 30 h to 25 °C.

The measured distribution of the remanent induction following the infiltration process (= heat treatment) resulted in a maximum value $B_{z,max}$ of 990 mT (Figure 4).

Drawings

Sheet 1 / 2

Increase of remanent induction by Yb- infiltration

Figure 1

Prior to infiltration

Figure 2

Following infiltration

Sheet 2/2

Figure 3

Prior to infiltration

Figure 4

Following infiltration